MOVPE of GaN on sapphire using the alternate precursor 1,1-dimethylhydrazine

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Abstract

To date, the most successful method to grow device-quality GaN epitaxial layers by metal-organic vapor-phase epitaxy (MOVPE) uses trimethyl (or triethyl) gallium (Me_3Ga/Et_3Ga) for the Ga source and ammonia (NH_3) for the N source. It is a high-temperature process with deposition temperatures typically in excess of $1000°C$ due to the high stability of the ammonia molecule. The use of a nitrogen precursor that decomposes at lower temperature is expected to result in a more efficient process and to allow growth of alloys at a lower temperature. The liquid precursor 1,1-dimethylhydrazine (Me_2NNH_2) has been tested as such an alternative precursor. GaN epilayers have been grown successfully on *c*-plane sapphire using low V/III ratio. The growth parameters and the characteristics of the grown epilayers are presented. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Due to its large and direct band gap, gallium nitride (GaN)-based III–V compound semiconductors have become the most promising materials for fabricating short-wavelength light-emitting diodes and optoelectronic devices (see Refs. [1–5]). The most successful method to grow device-quality GaN epitaxial layers by organometallic vapor-phase epitaxy (OMVPE) is a high-temperature reaction between trimethyl (or triethyl) gallium (Me_3Ga/Et_3Ga) and ammonia. However, this method is quite inefficient due to the high stability and volatility of the ammonia molecule, and reaction temperatures of $1000°C$ or higher with a very

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high V/III ratio (in general in excess of 4000) are required. Therefore, the use of a liquid-phase nitrogen precursor that decomposes at lower temperature and that allows the use of lower V/III ratios during growth is expected to result in a more efficient process that should also allow better control of the stoichiometry of the GaN. Lowering the decomposition temperature of the precursors should have the additional advantage of allowing low-temperature growth of GaN-based alloys such as GaInN or GaAsN which are less stable at high temperatures.

For the III–V semiconductors GaAs and InP, the gaseous hydrides arsine and phosphine have been successfully replaced by tertiarybutylarsine and tertiarybutylphosphine. However, for GaN, several authors have shown that the equivalent alkyl: tertiarybutylamine (TBAm), failed to produce GaN [6–8]. 1,1-Dimethylhydrazine (Me_2NNH_2), however, has already been used successfully as a liquid-phase nitrogen precursor for the growth of the cubic phase of GaN on GaAs [9,10] and for the growth of alloys (GaNInAs) at low temperatures [11,12]. The pyrolysis of Me_2NNH_2 and of its co-pyrolysis with trimethylgallium using an isothermal flow tube reactor at atmospheric pressure has been studied by Lee et al. [13].

In order to further understand the potential and limitations of Me_2NNH_2 as a nitrogen precursor for the growth of GaN and its alloys by OMVPE, and to determine potential adducts and other intermediates that could be formed during the deposition process using Me_2NNH_2 and Et_3Ga, direct chemical reactions between the two precursors have been studied. The results obtained have allowed the identification of a stable adduct and intermediate dimer [14]. To compare this data with the actual OMVPE process gasphase pyrolysis trials were undertaken for both Me_2NNH_2 and a Me_2NNH_2/Et_3Ga mixture [15]. Finally, GaN epilayers have been grown by MOVPE using the above source combination. The structural and optical characteristics of these films have been measured. These results are presented to demonstrate the high quality of the layers obtained and highlight the usefulness of this new precursor system.

2. Experimental procedure

Hydrazine and substituted hydrazines are available commercially. Hydrazine is very unstable and therefore difficult to handle for use in a OMVPE reactor; substituted hydrazines are less so. 1,1-Dimethylhydrazine (Me_2NNH_2) is more stable than hydrazine and monomethylhydrazine and it has a relatively high vapor pressure given by $\log P = 8.19–1780/T$ [15]. Me_2NNH_2 is hygroscopic and there have been concerns about its high water content that could lead to excess incorporation of oxygen when used for growth of GaN. This concern has been addressed and new purification techniques developed to allow low water content product to be produced [16].

Triethylgallium (Et_3Ga) was chosen for this study as the Ga precursor because it has been shown to produce material with lower carbon concentration when used for growth of several III–V compounds [17–19].

The GaN growth experiments were conducted in a low-pressure OMVPE vertical, cylindrical stainless-steel reactor equipped with a radiatively heated high-speed rotating wafer carrier. Pd-purified hydrogen was used as the carrier gas. Me_2NNH_2 and Et_3Ga were introduced in the reactor growth chamber through separate injector. During the experiments, the Me_2NNH_2 and Et_3Ga bubblers were held at a constant temperature of $0°C$ and $25°C$, respectively. Samples have been grown with a total pressure of the growth chamber from 60 to 350 Torr. The sapphire substrates were first cleaned in situ with pure hydrogen at $1000°C$ followed by nitridation of the surface under a flow of Me_2NNH_2 at $1000°C$. Deposition of a low-temperature GaN buffer layer was initiated with Et_3Ga and Me_2NNH_2 introduced simultaneously to the deposition chamber at temperatures in the range $500–620°C$. The flow of Et_3Ga was $7.8\,\mu mol/min$ and the molar ratio of V/III precursors was varied from 10 to 80. The temperature was then raised to deposit high-quality GaN in the range $800–1010°C$.

3. Results and discussion

Number of similarities have appeared comparing published data on the growth of GaN using

ammonia and the present growth data of GaN using Me_2NNH_2. We found that the samples deposited with Me_2NNH_2 follow a similar growth scheme, including similar temperature range, to that observed when using ammonia: first, a buffer layer is deposited at low temperature then the temperature is increased to the growth temperature. Stoichiometric GaN can be grown with Me_2NNH_2 starting at about 650°C; however, the obtained layers grow in three dimensions and are very rough. Smoothening due to a two-dimensional growth mode is obtained at 1000°C and above as will be described below. This is not surprising as the same result was observed for growth of other III–V compounds using sources other than hydride gases for the group V precursors. In general, the growth temperature is unchanged but the V/III ratio is significantly reduced when precursors that decompose at lower temperature are used. However, the result that GaN can be obtained at lower temperature is a significant result and points to the possibility of using Me_2NNH_2 for the growth of GaN-based alloys.

The main difference from growth with ammonia is the low V/III ratio which can be used. We find that a ratio of 50 gives GaN of good optical quality as revealed by photoluminescence (Fig. 1). This photoluminescence spectrum, recorded using a sample only 0.5 μm thick, exhibits the characteristic GaN I_2 peak at 3.475 eV with a FWHM of 18 meV.

Another difference is that the morphology of the high-temperature grown epitaxial layers is much less affected by the thickness of the buffer layer than it is when growth is carried out from ammonia. With our experimental set-up, the growth rate for the buffer layer did not vary with temperature in the range 560–620°C and was about 0.5 μm/h for a growth chamber pressure of 300 Torr. Buffer layers grown at 580°C were used in the growth experiments presented here. Buffer layers of thicknesses varying between 15 and 150 nm have been grown prior to the growth of the high-temperature epitaxial layer. Contrary to what is observed for growth with ammonia [3], the morphology of the high-temperature epitaxial layer is not affected by the thickness of the buffer layer. Fig. 2 is a cross-section TEM image of a GaN epitaxial layer grown on a very thick buffer. The dislocations density in
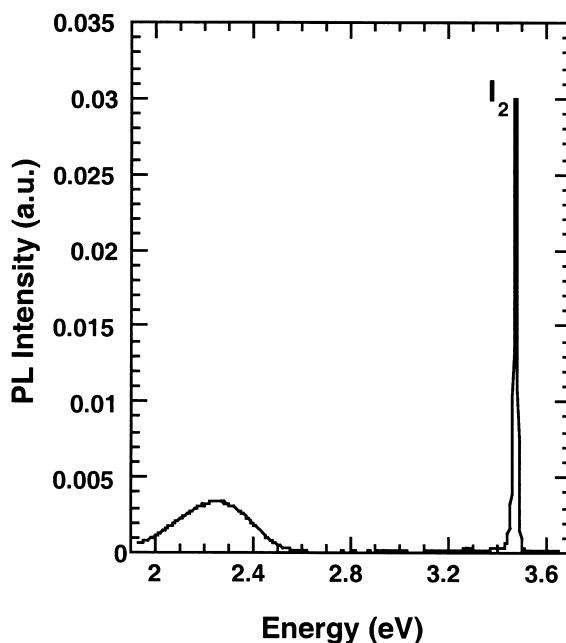

Fig. 1. Representative photoluminescence spectrum of a hexagonal GaN sample, 0.5 μm thick, grown with Me_2NNH_2.

the epitaxial layer is about $4 \times 10^9/cm^2$ which is similar to the dislocation density of layers grown with ammonia.

Fig. 2 reveals the presence of voids in the buffer layers. The density of these voids can be controlled by the total pressure in the growth chamber and by the flow of TEGa. The quality of the epitaxial layer starts deteriorating only for rather large densities of voids in excess of 40% of the surface area. For this large percentage, the epitaxial layer becomes discontinuous. For samples having a lower percentage of void areas in the buffer layer (<40%), it is particularly interesting to note that the region of the epilayer directly above the voids has a significantly lower density of dislocations than the region that grew in direct contact with the buffer layer. When the temperature is raised to the high growth temperature (1000°C for the sample shown in Fig. 2), growth occurs by lateral growth in two dimensions. Growth over the voids is initiated from islands of the buffer layer on their sides and proceed by lateral overgrowth in a strain-free environment (as seen from the facets developing around the
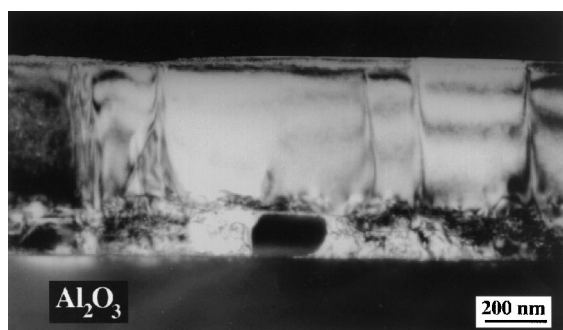
Fig. 2. Cross-section TEM image of a GaN epilayer grown on a thick buffer layer showing an area of low defect density above the void in the thick buffer layer.
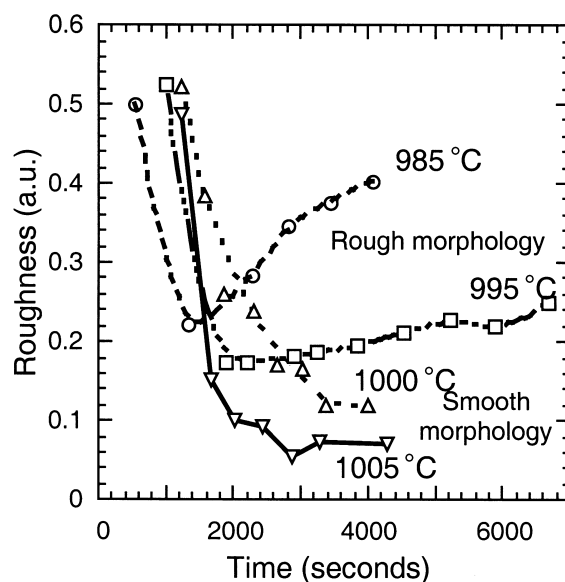

Fig. 3. Measurements of the amount of roughness of the epilayer after buffer growth (3D–2D transition) for GaN epilayer grown with Me_2NNH_2 at various temperatures.

voids yielding to the observed low dislocation density in these areas).

Another significant difference between growth of GaN with ammonia vs. growth with Me_2NNH_2 is seen in the thickness needed to recover from the three-dimensional growth mode of the buffer layer to the two-dimensional growth of the high-temperature layer. Using in situ laser interferometry [20] and the technique described in Ref. [21] we could calculate in real-time the amount of roughening/smoothening of the epilayers as the growth proceeds and determine the thickness needed to get a smooth surface. When three-dimensional growth occurs, the scattering of the probe wavelength increases and results in a decrease of the reflected intensity compared to the expected reflected intensity from a smooth epilayer grown in a two-dimensional growth mode. For a high-quality sample grown with ammonia that thickness needed to complete the transition from three-to two-dimensional growth and the production of smooth epilayers is about 1.5 µm. Fig. 3 shows in arbitrary scale the smoothening of the epilayers grown at various temperatures with Me_2NNH_2. We observed that smoothening of the epilayer occurs only starting at a growth temperature of 1000°C. At that temperature, a smooth surface is obtained after 0.5 µm of growth and at 1005°C, it is obtained after only 0.4 µm of growth. These values are 2–3 times smaller that the observed value in the ammonia process for high-quality growth. At temperatures below 1000°C, we observe an initial drop in the roughness of the sample due to the annealing of the

buffer layer at high temperature, but two-dimensional growth does not take place and the roughening due to three-dimensional growth increases as growth proceeds. A smaller transition region can be advantageous for device fabrication.

4. Conclusion

Me_2NNH_2 and Et_3Ga have been used to grow hexagonal GaN on sapphire c-plane substrates. We observe similarities with growth of GaN using ammonia in terms of growth scheme and temperatures. However, the process is much more efficient as a V/III ratio of only 50 is used compared to several thousands when ammonia is used. The process is also unaffected by the thickness of the buffer layer and smooth epilayers are obtained after only 0.5 µm of growth at high temperature.

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